

PATENT ABSTRACTS OF JAPAN

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LTD

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(54) ORGANIC ELECTROLYTIC SECONDARY BATTERY

(57)Abstract:

PURPOSE: To provide a highly reliable organic electrolytic secondary battery.

CONSTITUTION: In a battery having a negative electrode consisting of a carbon material capable of storing and releasing lithium, a positive electrode, and an organic electrolyte consisting of a solvent and a solute, a mixture of a cyclic carbonate and an acyclic sulfone is used for the solvent. Thus, the reduction in discharge capacity accompanying the progress of charge and discharge cycle which is a problem of batteries of this kind can be effectively suppressed.

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CLAIMS

[Claim(s)]

[Claim 1] The organic electrolytic-solution rechargeable battery which is a cell equipped with the negative electrode which consists of a carbon material in which the occlusion and discharge of a lithium are possible, a positive electrode, and the organic electrolytic solution which consists of a solvent and a solute, and is characterized by the aforementioned solvent containing annular carbonate and the un-annular sulfone.

[Claim 2] The organic electrolytic-solution rechargeable battery according to claim 1 whose annular carbonate is one or more sorts chosen from ethylene carbonate and propylene carbonate.

[Claim 3] The organic electrolytic-solution rechargeable battery of the claim 1 or 2 publications whose un-annular sulfones are one or more sorts chosen from a dimethyl sulfone, an ethyl methyl sulfone, and a diethyl sulfone.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the lithium cell which is the high-energy density as the power supply for a drive or memory maintenance power supply of electronic equipment, and has high reliability.

[0002]

[Description of the Prior Art] With the formation of small lightweight with rapid electronic equipment, to the cell which is the power supply, it is small, lightweight, and high-energy density, and the demand to development of the rechargeable battery in which repeat charge and discharge are still more possible is increasing. As a rechargeable battery which fills these demands, an organic electrolytic-solution rechargeable battery is the most promising.

[0003] Various things, such as lithium cobalt multiple oxides including 2 titanium sulfides, a spinel type lithium manganic acid ghost, a vanadium pentoxide, and a molybdenum trioxide, are examined by the positive active material of an organic electrolytic-solution rechargeable battery. Especially, a lithium cobalt multiple oxide (LiCoO_2) and a spinel type lithium manganic acid ghost (LiMn_2O_4) are using as a positive electrode, in order [more than 4V (Li/Li^+)] to perform charge and discharge by electropositive potential extremely, and the cell which has high discharge voltage can be realized.

[0004] As for the negative-electrode active material of an organic electrolytic-solution rechargeable battery, although various things, such as Li-aluminum alloys, carbon materials, etc. of a lithium including a metal lithium in which occlusion and discharge are possible, are examined, a carbon material has the advantage that a cell with a long cycle life with high and safety is obtained, especially.

[0005] However, in this seed cell, while making into a negative-electrode active material the lithium which has **** potential, in order to use the metallic oxide which has electropositive potential, it is in the situation that the electrolytic solution is easy to be decomposed in a negative electrode and each positive electrode in a positive electrode. Therefore, in selection of the electrolytic solution, it is indispensable to consider as the composition in consideration of these points, and using the various electrolytic solutions is proposed. For example, the mixed electrolytic solution (refer to JP,4-171674,A) with the electrolytic solution (refer to JP,3-152879,A), and the annular carbonate and chain-like carbonate containing a dimethyl sulfone etc. is raised.

[0006] On the other hand, generally as a solute, the lithium perchlorate, the trifluoromethane sulfonic-acid lithium, the 6 fluoride [phosphoric acid] lithium, etc. are used. A 6 fluoride [phosphoric acid] lithium is briskly used increasingly especially in recent years from the reason the ion conductivity of the electrolytic solution in which safety made it dissolve highly is high.

[0007] However, although the dimethyl sulfone had the thermal stability and the oxidation-resistant ability which were excellent in itself, by the cell which used for the negative electrode the carbon material in which the occlusion and discharge of a lithium are possible, a good charge-and-discharge cycle property was not acquired. On the other hand, although the mixed electrolytic solution of annular carbonate and chain-like carbonate showed the good cycle property under the room temperature, under the elevated temperature, degradation became large.

[0008]

[Means for Solving the Problem] this invention is a cell equipped with the negative electrode which consists of a carbon material in which the occlusion and discharge of a lithium are possible, a positive electrode, and the organic electrolytic solution which consists of a solvent and a solute, and the above-mentioned problem is solved by using the mixture of annular carbonate and an un-annular sulfone compound for the aforementioned solvent at least.

[0009] In addition, when using the high carbon material of a degree of graphitization for a negative electrode, it is desirable to use a dimethyl sulfone, an ethyl methyl sulfone, and a diethyl sulfone as an un-annular sulfone for obtaining the cell which is excellent in a high-rate-discharge performance in ethylene carbonate as annular carbonate.

[0010]

[Function] As mentioned above, by this seed cell, it is easy to produce the decomposition reaction of the electrolytic solution, and has become the main factor to which this degrades a cell performance. However, when the mixture of annular carbonate and an un-annular sulfone compound was used for the electrolytic solution, it excelled in the preservation property, and a cycle property also finds out that a good cell is obtained and came to complete this invention. Although this reason is not clear, it has guessed as following.

[0011] Since it is small compared with the molecule of annular carbonate, such as ethylene carbonate and propylene carbonate, the molecule of the un-annular sulfone represented by the dimethyl sulfone is easy to be incorporated between the layers of negative-electrode carbon with a lithium ion at the time of charge. The distance between layers of negative-electrode carbon is pushed up by it. Therefore, destruction of the layer structure of negative-electrode carbon progresses as the occlusion and discharge of the lithium ion by charge and discharge are repeated, and it is thought that the fall of cell capacity had arisen.

[0012] However, if annular carbonate and an un-annular sulfone are mixed like this invention, in order that annular carbonate may form the protective film of lithium ion conductivity in a negative-electrode carbon front face and may suppress incorporation of a between [the negative-electrode carbon layers of an un-annular sulfone molecule], destruction of the layer structure of negative-electrode carbon also comes to be suppressed. Furthermore, it is thought that the electrolytic solution of this invention shows the cycle performance which was excellent under the elevated temperature since the chain-like carbonate inferior to the stability under an elevated temperature was not contained.

[0013]

[Example] Although this invention is explained below using a suitable example, unless the meaning of this invention is exceeded, it is not limited to the following examples.

[0014] A positive electrode carries out pressurization molding, after mixing enough the carbon powder as a lithium cobalt multiple oxide (LiCoO_2) and an electric conduction agent, and the fluororesin powder as a binder by the weight ratio of 90:3:7. A negative electrode carries out pressurization molding, after mixing a graphite powder and the fluororesin powder as a binder enough by the weight ratio of 91:9.

[0015] Drawing 1 is 1 example cell of this invention. In this drawing, it is the obturation board which serves as the negative-electrode terminal into which the case which serves as the positive-electrode terminal which 1 pierced the stainless steel plate of electrolytic-solution-proof nature, and was processed, and the stainless steel plate as 1 with 2 [same] were pierced and processed, and the negative electrode 3 is contacted by the wall. The separator which consists of polypropylene into which 5 sank the organic electrolytic solution, and 6 are positive electrodes. The cell is carrying out sealing obturation by binding tight the periphery of the obturation board 2 which serves as a negative-electrode terminal the opening edge of the case 1 which serves as a positive-electrode terminal through a caulking and a gasket 4 to the inner direction.

[0016] What dissolved the 6 fluoride [phosphoric acid] lithium in the organic solvent which mixed ethylene carbonate and the dimethyl sulfone by the volume ratio 1:1 by the concentration of one mol/l. was used for the organic electrolytic solution. It did about 150microl pouring in of the above-mentioned electrolytic solution at the cell. This cell size is 2mm in the diameter of 20mm, and height. this invention cell was set to (A).

[0017] In the above-mentioned example, everything but having used the ethyl methyl sulfone and the diethyl sulfone, respectively set to (B) and (C) the cell of this invention considered as the same composition as this example instead of the dimethyl sulfone.

[0018] Everything but furthermore having used the mixture (volume ratio 1:1) of ethylene carbonate and diethyl carbonate for comparison made a (a) the comparison cell considered as the same composition as the cell of this invention.

[0019] Next, it is 300 cycle ***** about the charge-and-discharge cycle-life examination which discharges until it charges these cells by the 2.0mA constant current until terminal voltage results in 4.2V, and it continues and terminal voltage similarly amounts to 2.7V in a 2.0mA constant current in a thermostat with a temperature of 60 degrees C. Change of the service capacity accompanying advance of the charge-and-discharge cycle of each cell is shown in drawing 2.

[0020] the Ming kana from the result of drawing 2 — this invention cell (A) using the mixed solvent of annular carbonate and an un-annular sulfone, (B), and (C) have [like] the small fall of the service capacity accompanying advance of a charge-and-discharge cycle compared with a comparison cell (a)

[0021] In addition, although the above-mentioned example explained the case where ethylene carbonate was used as annular carbonate, if the high carbon material of a degree of graphitization is not used for a negative electrode, the mixed solvent of propylene carbonate, ethylene carbonate, and propylene carbonate can be used instead of ethylene carbonate.

[0022] In the above-mentioned example, especially although the case where annular carbonate and an un-annular sulfone were mixed by the volume ratio 1:1 was explained, it is not limited. The addition to the annular carbonate of these un-annular sulfones has desirable 20 - 80 volume % to both total amount. Because, it is to become easy to solidify the electrolytic solution at low temperature, if ethylene carbonate with the high congealing point is used when the content of a sulfone compound is under 20 volume %, and for the ion conductivity of the electrolytic solution to fall, if the content of a sulfone compound with a low dielectric constant exceeds 80% on the other hand.

[0023] Moreover, as a sulfone compound used by this invention, although at least one or more sorts, such as a dimethyl sulfone, an ethyl methyl sulfone, and a diethyl sulfone, can be used, for example, a dimethyl sulfone is the point of ion conductivity and an ethyl methyl sulfone is desirable especially in respect of low-temperature-performance ability.

[0024] Although the case where a lithium cobalt multiple oxide was used as a positive active material was furthermore explained in the above-mentioned example, it is not limited to especially this. Various things, such as manganese dioxide including 2 titanium sulfides and a lithium nickel multiple oxide (LiNiO_2), a spinel type lithium manganic acid ghost (LiMn_2O_4), a vanadium pentoxide, and a molybdenum trioxide, can be used.

[0025] Although this example explained the case where the mixed stock of annular carbonate and an un-annular sulfone was used for an organic solvent, it can add as the 3rd component and the organic solvent conventionally used with the lithium cell can be used. For example, chain-like carbonate, such as ether solvents, such as annular sulfur compounds, such as ester solvents, such as gamma-butyrolactone and a methyl fall mate, and a sulfolane, 1, 2-dimethoxyethane, and a tetrahydro furan, dimethyl carbonate, ethyl methyl carbonate, and diethyl carbonate, etc. is raised. As an electrolyte, one or more sorts, such as a lithium perchlorate, a 6 fluoride arsenic-acid lithium, 4 fluoride lithium borate, a trifluoromethane sulfonic-acid lithium, and a fluosulfonic-acid lithium, can be used.

[0026] In addition, although each cell concerning the aforementioned example is a coin form cell, the same effect is acquired even if it applies this invention to a cylindrical shape, a square shape, or a paper form cell.

[0027]

[Effect of the Invention] As mentioned above, in a cell equipped with the negative electrode which consists of a carbon material in which the occlusion and discharge of a lithium are possible, a positive electrode, and the organic electrolytic solution which consists of a solvent and a solute, the fall of the service capacity accompanying advance of the charge-and-discharge cycle which is the problem of this seed cell can be effectively suppressed by using the mixture of annular carbonate and an un-annular sulfone for the aforementioned solvent, and the industrial value is size very much.

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TECHNICAL FIELD

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EFFECT OF THE INVENTION

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TECHNICAL PROBLEM

[Description of the Prior Art] With the formation of small lightweight with rapid electronic equipment, to the cell which is the power supply, it is small, lightweight, and high-energy density, and the demand to development of the rechargeable battery in which repeat charge and discharge are still more possible is increasing. As a rechargeable battery which fills these demands, an organic electrolytic-solution rechargeable battery is the most promising.

[0003] Various things, such as lithium cobalt multiple oxides including 2 titanium sulfides, a spinel type lithium manganic acid ghost, a vanadium pentoxide, and a molybdenum trioxide, are examined by the positive active material of an organic electrolytic-solution rechargeable battery. Especially, a lithium cobalt multiple oxide (LiCoO_2) and a spinel type lithium manganic acid ghost (LiMn_2O_4) are using as a positive electrode, in order [more than 4V (Li/Li^+)] to perform charge and discharge by electropositive potential extremely, and the cell which has high discharge voltage can be realized.

[0004] As for the negative-electrode active material of an organic electrolytic-solution rechargeable battery, although various things, such as Li-aluminum alloys, carbon materials, etc. of a lithium including a metal lithium in which occlusion and discharge are possible, are examined, a carbon material has the advantage that a cell with a long cycle life with high and safety is obtained, especially.

[0005] However, in this seed cell, while making into a negative-electrode active material the lithium which has **** potential, in order to use the metallic oxide which has electropositive potential, it is in the situation that the electrolytic solution is easy to be decomposed in a negative electrode and each positive electrode in a positive electrode. Therefore, in selection of the electrolytic solution, it is indispensable to consider as the composition in consideration of these points, and using the various electrolytic solutions is proposed. For example, the mixed electrolytic solution (refer to JP,4-171674,A) with the electrolytic solution (refer to JP,3-152879,A), and the annular carbonate and chain-like carbonate containing a dimethyl sulfone etc. is raised.

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MEANS

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OPERATION

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[0012] However, if annular carbonate and an un-annular sulfone are mixed like this invention, in order that annular carbonate may form the protective film of lithium ion conductivity in a negative-electrode carbon front face and may suppress incorporation of a between [the negative-electrode carbon layers of an un-annular sulfone molecule], destruction of the layer structure of negative-electrode carbon also comes to be suppressed. Furthermore, it is thought that the electrolytic solution of this invention shows the cycle performance which was excellent under the elevated temperature since the chain-like carbonate inferior to the stability under an elevated temperature was not contained.

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EXAMPLE

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[0015] Drawing 1 is 1 example cell of this invention. In this drawing, it is the obturation board which serves as the negative-electrode terminal into which the case which serves as the positive-electrode terminal which 1 pierced the stainless steel plate of electrolytic-solution-proof nature, and was processed, and the stainless steel plate as 1 with 2 [same] were pierced and processed, and the negative electrode 3 is contacted by the wall. The separator which consists of polypropylene into which 5 sank the organic electrolytic solution, and 6 are positive electrodes. The cell is carrying out sealing obturation by binding tight the periphery of the obturation board 2 which serves as a negative-electrode terminal the opening edge of the case 1 which serves as a positive-electrode terminal through a caulking and a gasket 4 to the inner direction.

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[0017] In the above-mentioned example, everything but having used the ethyl methyl sulfone and the diethyl sulfone, respectively set to (B) and (C) the cell of this invention considered as the same composition as this example instead of the dimethyl sulfone.

[0018] Everything but furthermore having used the mixture (volume ratio 1:1) of ethylene carbonate and diethyl carbonate for comparison made a (a) the comparison cell considered as the same composition as the cell of this invention.

[0019] Next, it is 300 cycle ***** about the charge-and-discharge cycle-life examination which discharges until it charges these cells by the 2.0mA constant current until terminal voltage results in 4.2V, and it continues and terminal voltage similarly amounts to 2.7V in a 2.0mA constant current in a thermostat with a temperature of 60 degrees C. Change of the service capacity accompanying advance of the charge-and-discharge cycle of each cell is shown in drawing 2.

[0020] the Ming kana from the result of drawing 2 — this invention cell (A) using the mixed solvent of annular carbonate and an un-annular sulfone, (B), and (C) have [like] the small fall of the service capacity accompanying advance of a charge-and-discharge cycle compared with a comparison cell (a)

[0021] In addition, although the above-mentioned example explained the case where ethylene carbonate was used as annular carbonate, if the high carbon material of a degree of graphitization is not used for a negative electrode, the mixed solvent of propylene carbonate, ethylene carbonate, and propylene carbonate can be used instead of ethylene carbonate.

[0022] In the above-mentioned example, especially although the case where annular carbonate and an un-annular sulfone were mixed by the volume ratio 1:1 was explained, it is not limited. The addition to the annular carbonate of these un-annular sulfones has desirable 20 - 80 volume % to both total amount. Because, it is to become easy to solidify the electrolytic solution at low temperature, if ethylene carbonate with the high congealing point is used when the content of a sulfone compound is under 20 volume %, and for the ion conductivity of the electrolytic solution to fall, if the content of a sulfone compound with a low dielectric constant exceeds 80% on the other hand.

[0023] Moreover, as a sulfone compound used by this invention, although at least one or more sorts, such as a dimethyl sulfone, an ethyl methyl sulfone, and a diethyl sulfone, can be used, for example, a dimethyl sulfone is the point of ion conductivity and an ethyl methyl sulfone is desirable especially in respect of low-temperature-performance ability.

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[0025] Although this example explained the case where the mixed stock of annular carbonate and an

un-annular sulfone was used for an organic solvent, it can add as a third component and the organic solvent conventionally used with the lithium cell can be used. For example, chain-like carbonate, such as ether solvents, such as annular sulfur compounds, such as ester solvents, such as gamma-butyrolactone and a methyl fall mate, and a sulfolane, 1, 2-dimethoxyethane, and a tetrahydro furan, dimethyl carbonate, ethyl methyl carbonate, and diethyl carbonate, etc. is raised. As an electrolyte, one or more sorts, such as a lithium perchlorate, a 6 fluoride arsenic-acid lithium, 4 fluoride lithium borate, a trifluoromethane sulfonic-acid lithium, and a fluosulfonic-acid lithium, can be used.

[0026] In addition, although each cell concerning the aforementioned example is a coin form cell, the same effect is acquired even if it applies this invention to a cylindrical shape, a square shap , or a paper form cell.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is drawing having shown the internal structure of the button cell which is an example of an organic electrolytic-solution rechargeable battery.

[Drawing 2] It is the table having shown change of the service capacity accompanying advance of the charge-and-discharge cycle of an examination cell.

[Description of Notations]

- 1 Cell Case
 - 2 Obturation Board
 - 3 Negative Electrode
 - 4 Gasket
 - 5 Separator
 - 6 Positive Electrode
-

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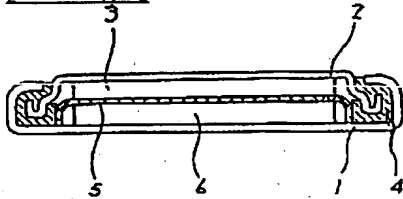
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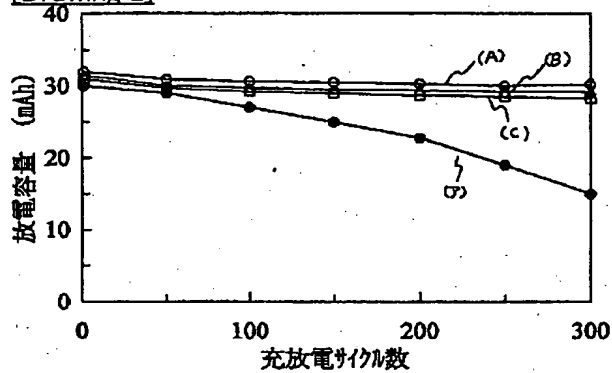
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DRAWINGS

[Drawing 1]



[Drawing 2]



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(19) 日本国特許庁 (J P)

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(22) 出願日 平成7年(1995)3月2日

(71) 出願人 000004282

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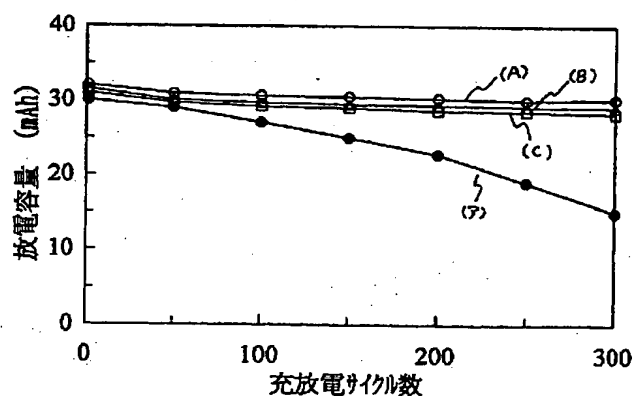
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(54) 【発明の名称】 有機電解液二次電池

(57) 【要約】

【目的】 信頼性の高い有機電解液二次電池を提供する。

【構成】 リチウムの吸蔵・放出が可能な炭素材料からなる負極と、正極と、溶媒と溶質からなる有機電解液とを備える電池において、前記溶媒に環状カーボネートと非環状スルホンとの混合物を用いることで、この種電池の問題である充放電サイクルの進行にともなう放電容量の低下を有効に抑制できる。



(2)

【特許請求の範囲】

【請求項1】 リチウムの吸蔵・放出が可能な炭素材料からなる負極と、正極と、溶媒と溶質からなる有機電解液とを備える電池であって、前記溶媒が環状カーボネートと非環状スルホンとを含有していることを特徴とする有機電解液二次電池。

【請求項2】 環状カーボネートが、エチレンカーボネート、プロピレンカーボネートから選ばれる1種以上である請求項1記載の有機電解液二次電池。

【請求項3】 非環状スルホンが、ジメチルスルホン、エチルメチルスルホン、ジエチルスルホンから選ばれる1種以上である、請求項1もしくは2記載の有機電解液二次電池。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、電子機器の駆動用電源もしくはメモリ保持電源としての高エネルギー密度でかつ高い信頼性を有するリチウム電池に関するものである。

【0002】

【従来の技術とその課題】電子機器の急激なる小形軽量化に伴い、その電源である電池に対して、小形で軽量かつ高エネルギー密度で、更に繰り返し充放電が可能な二次電池の開発への要求が高まっている。これら要求を満たす二次電池として、有機電解液二次電池が最も有望である。

【0003】有機電解液二次電池の正極活物質には、二硫化チタンをはじめとして、リチウムコバルト複合酸化物、スピネル型リチウムマンガン酸化物、五酸化バナジウムおよび三酸化モリブデンなどの種々のものが検討されている。なかでも、リチウムコバルト複合酸化物 (LiCoO_2) およびスピネル型リチウムマンガン酸化物 (LiMn_2O_4) は、4V (Li/Li^+) 以上のきわめて貴な電位で充放電を行うため、正極として用いることで、高い放電電圧を有する電池が実現できる。

【0004】有機電解液二次電池の負極活物質は、金属リチウムをはじめとして、リチウムの吸蔵・放出が可能な $\text{Li}-\text{Al}$ 合金や炭素材料など種々のものが検討されているが、なかでも炭素材料は、安全性が高くかつサイクル寿命の長い電池が得られるという利点がある。

【0005】しかし、この種電池において、卑な電位を有するリチウムを負極活物質とする一方、正極では貴な電位を有する金属酸化物を用いるため、負極、正極それぞれにおいて電解液が分解されやすい状況にある。従って、電解液の選択において、これらの点を考慮した構成とすることが必要不可欠であり、種々の電解液を用いることが提案されている。例えば、ジメチルスルホンを含む電解液 (特開平3-152879号公報参照) および環状カーボネートと鎖状カーボネートとの混合電解液 (特開平4-171674号公報参照) などがあげら

れる。

【0006】一方、溶質としては、過塩素酸リチウム、トリフルオロメタンスルホン酸リチウム、六フッ化リン酸リチウムなどが一般に用いられている。なかでも六フッ化リン酸リチウムは、安全性が高くかつ溶解させた電解液のイオン導電率が高いという理由から、近年盛んに用いられるようになってきている。

【0007】しかしながら、ジメチルスルホンはそれ自身優れた熱安定性、耐酸化性能を有するものの、リチウムの吸蔵・放出が可能な炭素材料を負極に用いた電池では、良好な充放電サイクル特性が得られなかった。一方、環状カーボネートと鎖状カーボネートとの混合電解液は、室温下では良好なサイクル特性を示したが、高温下では劣化が大きくなった。

【0008】

【課題を解決するための手段】本発明は、リチウムの吸蔵・放出が可能な炭素材料からなる負極と、正極と、溶媒と溶質からなる有機電解液とを備える電池であって、前記溶媒に少なくとも環状カーボネートと非環状スルホン化合物との混合物を用いることで上記問題を解決するものである。

【0009】なお、黒鉛化度の高い炭素材料を負極に用いる場合は環状カーボネートとしてエチレンカーボネートを、高率放電性能に優れる電池を得るには非環状スルホンとしてジメチルスルホン、エチルメチルスルホン、ジエチルスルホンを用いるのが好ましい。

【0010】

【作用】前述した如く、この種電池では電解液の分解反応が生じやすく、これが電池性能を劣化させる主因となっている。しかしながら、電解液に環状カーボネートと非環状スルホン化合物との混合物を用いると、保存特性に優れ、サイクル特性も良好な電池が得られることを見出し本発明を完成するに至った。この理由は明らかではないが、下記の如く推察している。

【0011】ジメチルスルホンに代表される非環状スルホンの分子は、エチレンカーボネート、プロピレンカーボネートなどの環状カーボネートの分子に比べ小さいため、充電時にリチウムイオンとともに負極炭素の層間に取り込まれやすい。それによって負極炭素の層間距離が押し上げられる。したがって、充放電によるリチウムイオンの吸蔵・放出を繰り返すにつれて負極炭素の層構造の破壊が進み、電池容量の低下が生じていたと考えられる。

【0012】しかし、本発明の如く環状カーボネートと非環状スルホンとを混合すると、環状カーボネートが負極炭素表面にリチウムイオン導電性の保護皮膜を形成し、非環状スルホン分子の負極炭素層間への取り込みを抑制するため、負極炭素の層構造の破壊も抑制されるようになる。さらに、本発明の電解液は、高温下での安定性に劣る鎖状カーボネートを含有しないため高温下にお

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いても優れたサイクル性能を示すものと思われる。

【0013】

【実施例】以下に、好適な実施例を用いて本発明を説明するが、本発明の趣旨を越えない限り、以下の実施例に限定されるものではない。

【0014】正極は、リチウムコバルト複合酸化物 (LiCoO_2) と導電剤としてのカーボン粉末および結着剤としてのフッ素樹脂粉末とを90:3:7の重量比で十分混合したのち、加圧成型したものである。負極は、黒鉛粉末と結着剤としてのフッ素樹脂粉末とを91:9

の重量比で十分混合したのち、加圧成型したものである。
【0015】図1は、本発明の1実施例電池である。この図において、1は耐電解液性のステンレス鋼板を打ち抜き加工した正極端子を兼ねるケース、2は1と同様のステンレス鋼板を打ち抜き加工した負極端子を兼ねる封口板であり、その内壁には負極3が当接されている。5は有機電解液を含浸したポリプロピレンからなるセパレーター、6は正極である。電池は、正極端子を兼ねるケース1の開口端部を内方へかしめ、ガスケット4を介して負極端子を兼ねる封口板2の外周を締め付けることにより密閉封口している。

【0016】有機電解液には、エチレンカーボネートとジメチルスルホンとを体積比1:1で混合した有機溶媒に、六フッ化リン酸リチウムを1モル/リットルの濃度で溶解したものをを用いた。電池には、上記電解液を約150 μl 注液した。この電池寸法は直径20mm、高さ2mmである。本発明電池を(A)とした。

【0017】上記実施例において、ジメチルスルホンの代わりに、それぞれエチルメチルスルホンおよびジエチルスルホンを用いたことの他は本実施例と同様の構成とした本発明の電池を(B)および(C)とした。

【0018】さらに比較のために、エチレンカーボネートとジエチルカーボネートとの混合物(体積比1:1)を用いたことの他は、本発明の電池と同様の構成とした比較電池を(ア)とした。

【0019】次に温度60℃の恒温槽中にて、これらの電池を2.0mAの定電流で、端子電圧が4.2Vに至るまで充電して、つづいて、同じく2.0mAの定電流で、端子電圧が2.7Vに達するまで放電する充放電サイクル寿命試験を300サイクルおこなった。各電池の充放電サイクルの進行にともなう放電容量の変化を図2に示す。

【0020】図2の結果から明かなように、環状カーボネートと非環状スルホンとの混合溶媒を用いた本発明電池(A)、(B)および(C)は、比較電池(ア)に比べ、充放電サイクルの進行にともなう放電容量の低下が小さい。

【0021】なお、上記実施例では、環状カーボネートとしてエチレンカーボネートを用いる場合を説明した

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が、負極に黒鉛化度の高い炭素材料を用いないのであれば、エチレンカーボネートの代わりにプロピレンカーボネートやエチレンカーボネートとプロピレンカーボネートとの混合溶媒を用いることができる。

【0022】上記実施例では、環状カーボネートと非環状スルホンとを体積比で1:1で混合した場合を説明したが特に限定されない。これらの非環状スルホンの環状カーボネートに対する添加量は、両者の含量に対して20~80体積%が望ましい。なぜならば、スルホン化合物の含有率が20体積%未満の場合は、凝固点の高いエチレンカーボネートを用いると電解液が低温で凝固しやすくなり、一方誘電率の低いスルホン化合物の含有率が80%を越えると電解液のイオン導電率が低下するためである。

【0023】また、本発明で使用されるスルホン化合物としては、例えばジメチルスルホン、エチルメチルスルホン、ジエチルスルホンなどの少なくとも1種以上を用いることができるが、なかでもジメチルスルホンがイオン導電率の点で、エチルメチルスルホンが低温性能の点で望ましい。

【0024】さらに上記実施例において、正極活物質としてリチウムコバルト複合酸化物を用いる場合を説明したが、特にこれに限定されない。二硫化チタン、リチウムニッケル複合酸化物(LiNiO_2)をはじめとして、二酸化マンガン、スピネル型リチウムマンガン酸化物(LiMn_2O_4)、五酸化バナジウムおよび三酸化モリブデンなどの種々のものを用いることができる。

【0025】本実施例では、有機溶媒に環状カーボネートと非環状スルホンとの混合系を用いる場合を説明したが、従来リチウム電池で用いられている有機溶媒を第3成分として添加して用いることができる。例えば、 γ -ブチロラクトン、メチルフォルメートなどのエステル溶媒、スルホランなどの環状硫黄化合物、1,2-ジメトキシエタン、テトラヒドロフランなどのエーテル溶媒、ジメチルカーボネート、エチルメチルカーボネート、ジエチルカーボネートなどの鎖状カーボネートなどがあげられる。電解質としては、過塩素酸リチウム、六フッ化砒酸リチウム、四フッ化ホウ酸リチウム、トリフルオロメタンスルホン酸リチウム、フルオロ硫酸リチウムなどの1種以上を用いることができる。

【0026】なお、前記の実施例に係る電池はいずれもコイン形電池であるが、円筒形、角形またはペーパー形電池に本発明を適用しても同様の効果が得られる。

【0027】

【発明の効果】上述したごとく、リチウムの吸蔵・放出が可能な炭素材料からなる負極と、正極と、溶媒と溶質からなる有機電解液とを備える電池において、前記溶媒に環状カーボネートと非環状スルホンとの混合物を用いることで、この種電池の問題である充放電サイクルの進行にともなう放電容量の低下を有効に抑制できるもので

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あり、その工業的価値は極めて大である。

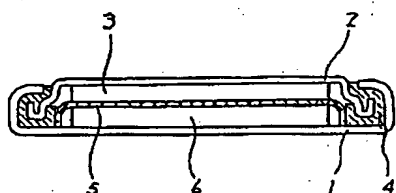
【図面の簡単な説明】

【図1】有機電解液二次電池の一例であるボタン電池の内部構造を示した図である。

【図2】試験電池の充放電サイクルの進行にともなう放電容量の変化を示した表である。

【符号の説明】

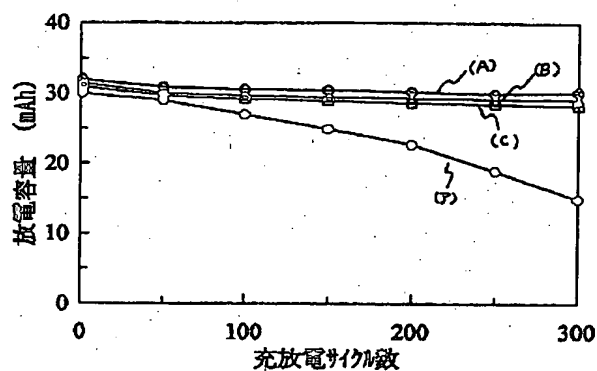
【図1】



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- 1 電池ケース
- 2 封口板
- 3 負極
- 4 ガスケット
- 5 セパレーター
- 6 正極

【図2】



【手続補正書】

【提出日】平成7年8月3日

【手続補正1】

【補正対象書類名】明細書

【補正対象項目名】図面の簡単な説明

【補正方法】変更

【補正内容】

【図面の簡単な説明】

【図1】有機電解液二次電池の一例であるボタン電池の内部構造を示した図である。

【図2】試験電池の充放電サイクルの進行にともなう放電容量の変化を示した図である。

【符号の説明】

- 1 電池ケース
- 2 封口板
- 3 負極
- 4 ガスケット
- 5 セパレーター
- 6 正極